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Forensic ballistics by inductively coupled plasma-optical emission spectroscopy: Quantification of gunshot residues and prediction of the number of shots using different firearms

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ABSTRACT

A new analytical method is proposed for the Pb, Ba and Sb quantifications on gunshot residues (GSR) from firearms using inductively coupled plasma optical emission spectrometry (ICP OES). Lead (Pb), barium (Ba) and antimony (Sb) concentrations in GSR from .38 revolver and .380 and .40 caliber pistols were determined as function of number of shots (from 1 to 5 for the .38 revolver and from 1 to 10 for the pistols) and multiple linear regression model was constructed to determine the number of shots. Also, the sensitivity of ICP OES was compared to conventional colorimetric test in function of distance of shooting (from 0 to 200 cm). Analyzing the effect of distance of shooting over the GSR concentration, the colorimetric test evidenced the presence of a red-pink color only at short distances (from 0 to 10 cm), thus indicating the presence of Pb. For ICP OES analyses, the two analytical methodologies employed presented higher sensitivity than the colorimetric assay, where Pb, Ba and Sb are found from 0 cm ([Pb] = 3158.63 μg L^{-1}; [Ba] = 85.33 μg L^{-1}; and [Sb] = 104.90 μg L^{-1}) to 200 cm ([Pb] = 81.52 μg L^{-1}; [Ba] = 20.20 μg L^{-1}; and [Sb] = 8.32 μg L^{-1}) for the extraction using digestion by microwave. For analyses of GSR using different firearms, good linear correlation coefficients ($R^2 > 0.97$) were observed between the GSR concentration and the number of shots. Therefore, it was possible to predict the number of shots with good accuracy from Pb, Ba and Sb concentrations using .38 revolver and .40 and .380 caliber pistols. Furthermore, the GSR concentration from different firearms, increased in the following order: .40 pistol > .380 pistol > 38 revolver.

1. Introduction

Violence affects directly the civil society. Firearms are used in 71% of all homicides in Brazil, corresponding to approximately 35 000 homicides per year. Two types of firearms basically have been developed and employed over the world. The revolver was firstly manufactured by Samuel Colt in 1835 and employs a practical of repeating and multishot firearm [1], being today, popularly used. In 1884, the first real fully automatic machine gun was patented by Sir Hiram Maxim. The development of the Maxim machine gun focused attention on the self-loading rifles and pistols. After, recoil-operated self-loading system was incorporated in the first multishot pistol in 1893 [1]. In Brazil the .40 caliber pistols are restricted to the police and the military.

Forensic ballistics represents a sub-area of criminalistics that includes the study of firearms and ammunition, in which the main goal is to relate the suspect to the murder weapon, most often through the ammunition. Firearm ammunition consists of the projectile, case, propellant and primer mixture; the last of which contains lead styphnate ($C_6HN_3O_8Pb$), barium nitrate, antimony trioxide, antimony tetroxide and aluminum [1,2].

During firing, a considerable amount of material in the gaseous or solid aerosol phase is produced and expelled along with the projectile. Part of the gaseous material solidifies, producing gunshot residues (GSR). GSR is composed of the elements lead, barium and antimony [4], which can be found primarily deposited on the shooter's hands, face and clothes; on people close to the firearm discharge; and even on the victim [3].

In Brazil, the colorimetric test utilizing the reagent sodium rhodizonate (Feigl-Suter Reaction) has been routinely used in GSR detection; however, this test only detects lead [5]. Despite its lower cost, one of the major problems with this test is contamination with other materials, which leads to false positive results. Another colorimetric

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test is based on the dermal nitrate test (also called the paraffin test), being one of the first color tests applied to determine the presence of GSR [6]. The paraffin test consists in pouring the hand of a suspected shooter in warm wax (paraffin) and treating the cooled cast for the presence of nitrites and nitrates using an acidic solution of diphenylamine. A positive result is produced when an instantaneous change to blue coloration is observed on the cast. A large number of sources present nitrites that may produce false positive reactions, making this method an unreliable indicator of GSR.

Recently, several studies have reported new analytical techniques for identifying firearms from GSR such as scanning electron microscopy/energy X-ray spectroscopy technique (SEM/EXS) [4,7–11], Raman spectroscopy [12,13], X-ray fluorescence (XRF) [10], inductively coupled plasma mass spectrometry (ICP-MS) [14,15], and inductively coupled plasma optical emission spectrometry (ICP OES) [3,16]. SEM/EXS [7,8] has been used and supported by a large number of experts because it allows for the correlation of the morphology and chemical composition of individual particles composed of Pb, Ba and Sb [17]. However, in July 1998, the Brazilian Cartridge Company (CBC) started the production and marketing of clean range ammunition. This ammunition contains a primer composed of the non-heavy metals Ti, Cu and Zn, and the projectiles are completely covered, thereby preventing any contamination with Pb. The use of the clean range ammunition has made the SEM/EXS technique ineffective, as no spherical particles containing Pb/Ba/Sb are produced by this ammunition when fired [18]. Furthermore, SEM/EXS requires a considerable amount of analyst time and expensive maintenance, and therefore, its implementation as a routine technique in forensic laboratories has come into question. Other analytical tools that have been highlighted in forensic ballistics are the ICP OES and ICP MS techniques.

ICP-MS and ICP OES present higher sensitivity than XRF (from mg g^{-1} to ng g^{-1}); thus, these techniques appear to be more promising and versatile. In 2003, Reis and collaborators [19] reported a new methodology for the recovery and analysis of GSR containing Pb, Ba and Sb based on the use of a swab moistened with a 2% (v/v) EDTA solution and ICP-MS. Maxima and minima concentrations of 7250 and 1.05; 108 and 0.72; and 482 and 1.25 mg L^{-1} were found for Pb, Sb and Ba, respectively, after one shot from a .38 caliber revolver. In 2004, Ulrich et al. [14] used the technique of ICP-MS to determine trace elements (Pb, Ba and Sb) in real samples of crimes involving .22 pistols. In 2007, Sarkis et al. [15] used the ICP-MS technique to describe the Pb, Ba and Sb concentrations from GSR of .38 revolver and .40 pistols. Despite the high sensitivity of the ICP-MS technique, its high installation and maintenance costs have made its implementation difficult.

The ICP OES technique had also been promising and versatile in GSR analyses. It is due to its lower price of installation and maintenance in relating to ICP-MS [20]. Romão et al. [2] show the development of a new analytical method from ICP OES for the collection and quantification of GSR. Pb, Ba and Sb concentrations from .38 caliber Taurus revolvers were monitored, and important parameters were evaluated, such as the collection region of the hand of the shooter; tape-type versus swabs collectors, and GSR quantification from the right and left hands. Within this context, the ICP OES technique is applied to evaluate the Pb, Ba and Sb quantifications of GSR produced in both shooter hands (right and left) using different firearms (revolver and pistols). The number of shots (from one to seven and ten shots) has been estimated. Also, the sensitivity of two different analytical tests was evaluated (colorimetric and ICP OES) in function of distance of shooting (from 0 to 200 cm).

2. Experiments

2.1. Materials and reagents

The collection of GSR was performed in the Ballistic Laboratory of the Criminal Institute of Vitória City, Espirito Santo state, Brazil. GSR samples were obtained by means of a single volunteer. The collections were performed from two hand regions: the thumb and forefinger palm (TF-palm) and thumb and forefinger back (TF-back). The shots were performed in duplicate. The firearms used were a Taurus® .38 caliber revolver and Taurus® and Imbel® pistols (.40 and .380 calibers, respectively). Other specifications are detailed in Table 1.

Nitric acid (HNO_3) of suprapure quality (65%, Merck, Germany), ultrapure water (with resistance > 18 M Ω·cm), prepared by a reverse osmosis system (Purelab Mk2 Ultra, UK), hydrogen peroxide (Cromoline Fine Chemicals, Brazil), and ethylenediaminetetraacetic acid (EDTA, Sigma-Aldrich, USA) were used. The EDTA was used as a complexing agent on moistened swabs. All reagents and solvents were used as received. A stock multielemental solution containing 1000 mg L^{-1} of the standards Ba, Sb and Pb (Sigma Aldrich, Switzerland) was serially diluted (100, 200, 300 to 500 μg L^{-1}) to form the calibration curve. All standard solutions were acidified with 2% HNO_3.

2.2. Instrumentation

An ICP OES (PerkinElmer, Model Optima 7000, USA) was used for the quantification of Pb, Ba and Sb. A Meinhard concentric nebulizer and cyclonic spray chamber with peristaltic pumping were used for introducing the samples into the plasma torch. The operating parameters were optimized using a central composite design. The optimized operating parameters, as well as the values of the limit of detection (LOD), limit of quantification (LOQ) and correlation factor of linear curve for the analytes Pb, Ba and Sb, are shown in Table 2.

After the collection step, the samples were digested in an ultrasonic bath (Unique, Model UltraCleaner 1450, Brazil) and in a microwave (CEM, Model Xpress, USA).

2.3. GSR detection in function of the shooter distance

To evaluate the sensitivity of technique of ICP OES and of the colorimetric test in function of shooter distance, a .38 Taurus® caliber revolver was used and the GSR was then collected over the target surface of 225 cm^2, which was made of white cotton. A single shot was performed and the distance between the shooter and target ranged in the following order: 0, 5, 10, 50, 100 and 200 cm (see in Fig. 1). After the shooting, an area of 64 cm^2 was removed and analyzed by colorimetric test using sodium rhodizonate reagent and ICP OES. The last, two collection methodologies were employed: the use of swab collectors and digestion using microwave. The target was substituted by a clean after each experiment, thus avoiding, an accumulative contamination which could affect the final quality of the results.

2.3.1. Colorimetric test

The colorimetric test was performed according to Feigl-Suter reaction [21]. Initially, a buffer solution containing sodium bicarbonate and tartaric acid (being prepared with approximately ca. 1.9 g of sodium tartrate and 1.5 g of tartaric acid dissolved in 100 mL of ultrapure water) of pH ≅ 3 was sprayed on the surface of the cotton target. After, a solution of 0.2 w/v % of sodium rhodizonate reagent was also sprayed. Positive results are obtained only for Pb from visual detection of a red-pink color.

Table 1
Specifications of the firearms used.

Firearm	Brand	Model	Caliber	Cartridge
Revolver	Taurus®	RT 85	.38	CBC .38 CHOG
Pistol	Imbel®	GC MD1	.380	CBC .380 ETOG
Pistol	Taurus®	PT 100 AFS	.40	CBC .40 ETPP